PATENT ABSTRACTS OF JAPAN

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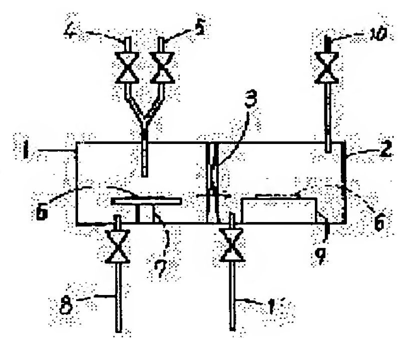
(54) FORMING METHOD FOR SILICON FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for forming a silicon film at a high speed and at a low temperature.
SOLUTION: The silicon film is formed by applying and thermally decomposing the mixture of a solution of higher-order silane and catalysis on a substrate 6. As the higher-order silane, higher-order silane expressed by a general formula of SinH2n+2 [(n) is an integer of n≥3] or haloganated higher-order silane expressed by a general formula of SinH1Xn [X is any one of chlorine, fluorine and iodine on the condition of 1+m=2n+2, and (n) is an integer of n≥3] is used. As a catalysist, a substance composed of a material or solution containing nickel, iron, cobalt and platinum is used.



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CLAIMS

[Claim(s)]
[Claim 1] The formation approach of the silicon film characterized by pyrolyzing the mixture of the solution of a high order silane, and a catalyst, and forming the silicon film on a substrate.
[Claim 2] The formation approach of the silicon film characterized by photodissociating the mixture of the solution of a high order silane, and a catalyst by irradiating the light of wavelength shorter than 400nm, and forming the silicon film on a substrate.
[Claim 3] Said high order silane is the formation approach of the silicon film according to claim 1 or 2 characterized by being the high order silane expressed with general formula SinH2n+2 (n is the integer of n>=3), or the halogenation high order silane expressed with a general formula SinHlXm (X is either chlorine, a fluorine, a bromine or iodine, and l+m=2n+2 and n are the integer of n>=3).
[Claim 4] Said catalyst is the formation approach of the silicon film according to claim 1 or 2 characterized by consisting of the matter or solution containing at least one of nickel, iron, cobalt, or the platinum.
[Claim 5] The solvent of said catalyst is the formation approach of the silicon film according to claim 4 characterized by the boiling point being a solvent lower than the temperature at the time of formation of the silicon film with a meltable high order silane.
[Claim 6] The formation approach of the silicon film according to claim 1 to 5 characterized by applying mixture with large catalyst concentration on a substrate, forming a crystalline-nucleus generating layer and applying mixture with small catalyst concentration on this.
[Claim 7] The formation approach of the silicon film according to claim 1 to 6 characterized by supplying atom-like hydrogen gas to a substrate a pyrolysis or in case it photodissociates.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the formation approach of the silicon film used for semiconductor devices, such as a solar battery and a thin film transistor.
[0002]
[Description of the Prior Art] the former — formation at the low temperature of the polycrystalline silicon (henceforth "poly-Si") film, or the amorphous silicon (henceforth "a-Si") film — plasma CVD (Chemical Vapor Deposition) — law, the heat CVD method, or the optical CVD method is used. equipment complicated [the RF generator which powder is generated in a gaseous phase with a slow membranous formation rate, and generally pollutes equipment with the plasma-CVD method from a gaseous phase], and expensive is required -- etc. -- there is a problem. Moreover, in the heat CVD method from a gaseous phase, when performing membrane formation of about several micrometers at high speed, it is necessary to form membranes at temperature higher than 600 degrees C, and an expensive heat-resistant thing must be used for a substrate.
[0003] Moreover, although there is also a method (refer to JP,6-244103,A) of making metals other than the above-mentioned approach, such as nickel, into a catalyst, and carrying out solid phase crystallization of a-Si at low temperature, since the membranous formation rate is slow, it is not suitable for formation of a thick film.
[0004] Then, the approach (refer to JP,5-144741,A) of applying high order silane liquid to a substrate, and forming membranes by ultraviolet radiation exposure as the film formation approach from the liquid phase which cancels these faults, and the approach (refer to JP,7-267621,A) of forming membranes by passing through the heat history which applies high order silane liquid to a substrate, and includes a temperature up process are proposed.
[0005] However, by these approaches, if the temperature of a substrate is set as suitable membrane formation temperature, since the boiling point of a high order silane is low, before (Table 1 Reference) and a polymerization are completed, a high order silane will evaporate, and formation of the thick film and adjustment of desired thickness will become difficult from 1 micrometer.
[0006]
[Table 1]

	SiH_4	Si_2H_6	Si_3H_8	n-Si_4H_{10}	n-Si_5H_{12}	n-Si_6H_{14}	n-Si_7H_{16}
融点(℃)	-185	-132.5	-117.4	-89.9	-72.2	-44.7	-30.1
沸点(℃)	-111.9	-14.5	52.9	108.1	153.2	193.6	226.8

[0007] The approach of generally forming membranes from the liquid phase by applying high order silane liquid can be formed at a high speed compared with the approach of forming membranes from a gaseous phase. However, as mentioned above, since a high order silane has the low boiling point, high order silane liquid evaporates at the time of membrane formation, the formed film cannot become quite thinner than spreading thickness, and it cannot obtain

thickness of arbitration. For this reason, to form membranes at a high speed and to raise the reactivity in low temperature was desired.
[0008] Moreover, in order to form the crystalline good crystal silicon film in a high speed comparatively, generally it is necessary to form membranes at temperature higher than 600 degrees C. However, if it is, for example, going to use the cheap substrate which consists of alkali free glass etc., since a problem is in thermal resistance, membranes must be formed at temperature lower than 600 degrees C, and the crystalline good crystal silicon film cannot be obtained.
[0009] Then, the purpose of this invention is offering the approach of forming the silicon film at low temperature at high speed, after maintaining the quality as a device in view of the above-mentioned trouble.
[0010]
[Means for Solving the Problem] The technical-problem solution approach by this invention pyrolyzes the mixture of the solution of a high order silane, and a catalyst, and forms the silicon film on a substrate. Moreover, the above-mentioned mixture is photodissociated by irradiating the light of wavelength shorter than 400nm, and the silicon film is formed on a substrate.
[0011] What is necessary is just to use the high order silane expressed with general formula SinH2n+2 (n is the integer of n>=3), or the halogenation high order silane expressed with a general formula SinHlXm (X is either chlorine, a fluorine, a bromine or iodine, and l+m=2n+2 and n are the integer of n>=3) as a high order silane. Moreover, in the case of a solution, the boiling point should be just lower [the solvent of a catalyst] than the temperature at the time of formation of the silicon film meltable [a high order silane] using what consists of a catalyst containing at least one of nickel, iron, cobalt, or the platinum, or a solution of this catalyst as a catalyst. According to this approach, the decomposition reaction of the silane can be carried out according to an operation of a catalyst, and the silicon film of desired thickness can be formed at low temperature at high speed than before.
[0012] A good crystal can be grown up, if mixture with large catalyst concentration is applied on a substrate, a crystalline-nucleus generating layer is formed and mixture with small catalyst concentration is especially applied on this in formation of the crystal silicon film.
[0013] Moreover, if atom-like hydrogen gas is supplied to a substrate a pyrolysis or in case it photodissociates, promotion of a polymerization and improvement in membraneous quality can be aimed at.
[0014]
[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to a detail.
[0015] In order to form the silicon film by this invention, the mixture of the solution of a high order silane and a catalyst is first applied to substrates, such as glass placed into the inert gas ambient atmosphere. Or you may make it apply the mixture of the solution of a high order silane, and the solution of a catalyst.
[0016] As a high order silane, what is expressed with general formula SinH2n+2 (n is the integer of n>=3) is used. Specifically They are trishiran (Si3H8), a tetra-silane (Si4H10), a PENTA silane (Si5H12), a hexa silane (Si6H14), a hepta-silane (Si7H16), an OKUTA silane (Si8H18), a nona silane (Si9H20), etc. Are expressed with a general formula SinHlXm (X is either chlorine, a fluorine, a bromine or iodine, and l+m=2n+2 and n are the integer of n>=3) instead of a high order silane, for example, you may be halogenation high order silanes, such as a chlorination PENTA silane. Moreover, a high order silane or two or more sorts of halogenation high order silanes may be used.
[0017] Moreover, what the matter containing at least one of nickel, iron, cobalt, or the platinum or its solution is used as a catalyst, and is specifically dissolved in an organic solvent at the presentation of the organic salt of nickel, a halogenation salt, etc. including nickel is desirable.
[0018] Since it is dangerous, holding a reactant high condition uses the organic solvent of a catalyst, and it should just make it mix in introductory tubing or on a substrate here, although it is possible to mix a high order silane and a catalyst directly. The organic solvent in this case has a meltable high order silane, its reactivity with a high order silane is low, and the boiling point is a

solvent lower than the boiling point of the high order silane used desirably lower than membrane formation temperature.
[0019] Although a catalyst and an organic solvent can set the combination as arbitration, as an example of a catalyst, nickel fluoride, a nickel chloride, nickel nitrate, nickel acetate, or nickel carbonate is mentioned. As an example of an organic solvent, moreover, a pentane, a hexane, a cyclohexane, The hydrocarbons expressed with CaHb(s) (5<=a<=10, 12<=b<=24), such as a heptane, an octane, an isooctane, benzene, ethylbenzene, toluene, or a xylene, diethylether, The ether and the ketones which are expressed with CaHbOc(s) (1<=a<=8, 4<=b<=14, 1<=c<=3), such as diisopropyl ether, an acetone, a methyl ethyl ketone, a methanol, ethanol, propanol, or a butanol, or alcohols is mentioned.
[0020] Moreover, the larger one of the high order silane concentration of the mixed liquor of a high order silane and a catalyst than 50 % of the weight is desirable. Since an organic solvent remains by making high order silane concentration as high as possible, the amount of the carbon incorporated in the film and oxygen can be lessened.
[0021] There is a spin coat method, a dip coating method, a spray coating method, the bar coat method, or the curtain coat method in the approach of applying a high order silane on a substrate. In the case of the spin coat method generally used, the rotational frequency of a spinner uses 300 - 6,000rpm preferably 100 to 10,000 rpm. Moreover, at this time, or it heats to the temperature higher than the boiling point of an organic solvent as spreading pretreatment, it evaporates an organic solvent beforehand and it removes an organic solvent, the polymerization of the high order silane may be carried out in part by approaches, such as an optical exposure, and you may process raising the viscosity of a high order silane etc.
[0022] Next, the predetermined silicon film is formed by the pyrolysis by heating, or the photolysis by the exposure of light. There are heating at the heater with which the base holding a substrate was equipped as the approach of heating, heating by the infrared lamp, etc. Moreover, by the approach of the photolysis by the exposure of ultraviolet radiation, it carries out in the gas ambient atmosphere where high order silanes, such as helium, neon, an argon, nitrogen, or hydrogen, are inactive. In order that a high order silane may absorb energy and may decompose as the light source of light to irradiate, the light source of ultraviolet radiation with wavelength shorter than 400nm is used. The discharge light of rare gas, such as for example, low-pressure mercury lamp light, hydrogen and heavy hydrogen or an argon, a krypton, and a xenon, excimer laser light, etc. are used for this.
[0023] If the above-mentioned approach is used, the decomposition reaction of the silane can be carried out according to an operation of a catalyst, and the silicon film can be formed at low temperature at high speed than before. In this case, if substrate temperature is higher than about 150 degrees C, the a-Si film will be obtained, and if still higher than about 500 degrees C, the poly-Si film can be obtained. In addition, the thickness of the silicon film obtained can be set as arbitration to about 5-50 micrometers by choosing the applying method.
[0024] Although the nickel mixed to a high order silane on the other hand functions as reducing the decomposition temperature of a silane, it is not desirable as a semiconductor material. For example, when using it as a solar battery, as for the nickel concentration in the film, it is desirable that it is lower than 1x1019-/cm3. It is more desirable 10-2 to 10-8 and to adjust smaller than especially 10-5 the nickel/Si ratio after dissolving the catalyst of a minute amount in an organic solvent and mixing with a high order silane especially.
[0025] Moreover, although the crystal grows from the crystalline nucleus which exists in early stages of membrane formation at the time of formation of the crystal silicon film, crystallinity will be affected when generating of a crystalline nucleus is controlled. Then, as shown in drawing 2 , on Substrate A, mixed liquor with large catalyst concentration (nickel/Si>=10-5) is applied, the 1st spreading layer B (crystalline-nucleus generating layer) is formed, and a crystalline nucleus is generated. Next, on the 1st spreading layer B, mixed liquor with small catalyst concentration (nickel/Si<10-5) is applied, and the 2nd spreading layer C is formed. The part used as the nucleus of the crystal growth to the direction of an arrow head can be restricted to the interior of the 1st spreading layer B by this, and crystalline improvement can be aimed at.
[0026] Furthermore, since a defect arises by the desorption of hydrogen at the time of the

membrane formation in an elevated temperature, it decompresses to 0.01 – 10Torr extent at the time of a temperature up, and atom-like hydrogen gas is supplied to a substrate. In order to obtain the hydrogen of the shape of this atom, metals, such as an approach of obtaining hydrogen gas by high frequency discharge, such as microwave, the approach of acquiring by irradiating high energy lines, such as ultraviolet rays, at hydrogen gas, and a tungsten, are heated, and there is the approach of acquiring by contact on that front face etc. By these approaches, promotion of a polymerization and improvement in membraneous quality can be aimed at.
[0027]
[Example] The example and the example of a comparison which enforced the approach of this invention and formed the silicon film hereafter are explained. Measurement shown below about the physical properties of the film formed in each example and the example of a comparison is performed, and this measurement result is shown in Table 2.
[0028] 1. Photoconductivity (A. M.1.5 or 100MW Exposure)
2. Dark Conductivity 3. Optical Gap [0029]
[Table 2]

	触媒		コート条件	膜質			
	濃度 (ppm)	量 (ml)		膜厚 (Å)	光導電率 (S/cm)	暗導電率 (S/cm)	光学ギャップ(eV)
実施例1	0.36	0.1	300rpm、10秒	1000	5×10^{-6}	5×10^{-10}	1.65
実施例2	0.36	0.1	300rpm、10秒	800	2×10^{-4}	1×10^{-4}	1.25
実施例3	0.36	0.1	300rpm、10秒	1400	2×10^{-6}	2×10^{-10}	1.63
実施例4-1	36	1.0	2000rpm、10秒	—	—	—	—
実施例4-2	0.36	0.1	100rpm、3秒	4500	3×10^{-4}	8×10^{-5}	1.20
実施例5	0.36	0.1	300rpm、10秒	1500	3×10^{-6}	3×10^{-10}	1.70
実施例6	0.36	0.1	300rpm、10秒	700	3×10^{-6}	1×10^{-10}	1.72
実施例7	0.36	0.1	スプレーコート	15000	5×10^{-6}	4×10^{-10}	1.64
比較例1	—	—	300rpm、10秒	成膜不可			
比較例2	—	—	300rpm、10秒	1000	5×10^{-6}	1×10^{-8}	1.50

[0030] The configuration of the experimental device of an example 1 is shown in <example 1> drawing 1 . This experimental device is equipped with the spreading room 1 and the membrane formation room 2, and these are connected through the gate valve 3. The spreading room 1 is equipped with the spin coater 7 and exhaust air Rhine 8 which are rotated by the motor which does not hold and illustrate dropping Rhine 5 for making dropping Rhine 4 for making the solution of a high order silane dropped, and the solution of a catalyst dropped, and a substrate 6. It is combined in the middle of Rhine, and dropping Rhine 4 and 5 is led to the spreading room 1 as one Rhine. Moreover, the membrane formation room 2 is equipped with gas supply Rhine 10 and exhaust air Rhine 11 for supplying the heating heater 9 for heating a substrate 6, inert gas, etc.
[0031] In this example, what dissolved nickel fluoride in diethylether as a catalyst was used, using a PENTA silane (Si5H12) as a high order silane.
[0032] Hereafter, the formation procedure of the silicon film is explained. 0.5ml of solutions of a PENTA silane was dropped at the substrate 6 from dropping Rhine 4, and 0.05-0.5ml of solutions of nickel fluoride was made dropped from dropping Rhine 5 at the spreading room 1. And a predetermined rotational frequency or predetermined carried out time amount rotation of the spin coater 7, and the spreading film was formed. In addition, the solution of the nickel fluoride mixed to PENTA silane 1ml at this time and the monograph affair of a spin coat are shown in Table 2.
[0033] Next, the membrane formation room 2 was introduced to 1x10-6Torr, and gaseous helium was introduced from gas supply Rhine 10 to 760Torr(s) after evacuation. Carrying out 0.5 l/min installation of the gaseous helium for a substrate 6 after migration through a gate valve 3 at the

membrane formation room 2, the temperature up of the substrate 6 was carried out until it became 200 degrees C at a rate of 100 degrees C/m at the heating heater 9, substrate temperature was held for 20 minutes, and the a-Si film was formed on the substrate 6.
[0034] Carried out the temperature up of the <example 2> substrate 6, and it was heated for 60 minutes until it became 500 degrees C at a rate of 100 degrees C/m at the heating heater 9, and also it was made the same as an example 1, and the poly-Si film was formed.
[0035] The chlorination PENTA silane was used as a <example 3> high order silane, and also it was made the same as an example 1, and the a-Si film was formed.
[0036] The temperature up was carried out until it applied mixture with large catalyst concentration, it formed the 1st spreading layer B and it became 500 degrees C at a rate of 100 degrees C/m, as shown in <example 4> drawing 2 , and it heated for 10 minutes, and the crystalline nucleus was formed (Table 2 four to example 1 reference). furthermore -- until it becomes temperature lower than 100 degrees C -- Substrate A -- mixture with small after cooling and catalyst concentration -- applying -- the 2nd spreading layer C -- forming -- 100 degrees C/m -- the temperature up was carried out until it came out comparatively and became 500 degrees C, and it heated for 60 minutes -- others (Table 2 four to example 2 reference) -- it was made the same as an example 1, and the crystalline good crystal silicon film was formed.
[0037] As shown in <example 5> drawing 3 , instead of pyrolyzing, using the experimental device which formed the low-pressure mercury lamp 12 in the membrane formation room 2 as the light source, irradiated light with wavelength shorter than 400nm from the low-pressure mercury lamp 12, and the photolysis was carried out, and also it was made the same as an example 1, and the a-Si film was formed.
[0038] As shown in <example 6> drawing 4 , using the experimental device equipped with the microwave generating room 14 established in the membrane formation room 2 in the middle of hydrogen gas installation Rhine 13 and its Rhine 13, it decompressed to 1Torr at the time of a temperature up, and the atom-like hydrogen gas with which energy was given with the microwave generated from the microwave generating room 14 was supplied on the substrate 6, and also it was made the same as an example 1, and the a-Si film was formed.
[0039] As shown in <example 7> drawing 5 , it applied with the spray coating method by emitting a solution at the tip of the spreading room 1 side of dropping Rhine 4 and 5 with a spray gun 15 using the experimental device which formed the spray gun 15, and also it was made the same as an example 1, and the a-Si film was formed.
[0040] The silicon film was not formed, although only the solution of a high order silane was applied, without mixing the <example 1 of comparison> catalyst and also it was made the same as an example 1.
[0041] Only the solution of a high order silane was applied, without mixing the <example 2 of comparison> catalyst, and also it was made the same as an example 2, and the a-Si film was formed.
[0042] When a catalyst was not mixed like the examples 1 and 2 of a comparison from the above result, as for the silicon film, membrane formation temperature was not formed at about 200 degrees C, but the a-Si film was formed for membrane formation temperature at about 500 degrees C. On the other hand, in the membrane formation conditions especially same in the example 2 as the example 2 of a comparison, the poly-Si film was formed of the operation of a catalyst, conductivity improved, and the optical gap decreased. Moreover, in the example 4, crystallization was promoted, the crystalline good silicon film was formed, and conductivity and an optical gap improved.
[0043] In addition, this invention is not limited to the above-mentioned operation gestalt, and can add many corrections and modification to the above-mentioned operation gestalt within the limits of this invention.
[0044]
[Effect of the Invention] As mentioned above, according to this invention, the solution and catalyst of a high order silane can be mixed and the a-Si film, the poly-Si film, or the crystalline good crystal silicon film can be formed at low temperature according to an operation of a catalyst a pyrolysis or by photodissociating at high speed than before.

[0045] Moreover, a cheap substrate is employable by low-temperature-izing membrane formation temperature by this approach.
[0046] If mixture with large catalyst concentration is applied on a substrate, a crystalline-nucleus generating layer is formed and mixture with small catalyst concentration is especially applied on this in formation of the crystal silicon film, crystalline improvement in the crystal silicon film can be aimed at.
[0047] Moreover, if atom-like hydrogen gas is supplied to a substrate a pyrolysis or in case it photodissociates, promotion of a polymerization and improvement in membraneous quality can be aimed at.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the formation approach of the silicon film used for semiconductor devices, such as a solar battery and a thin film transistor.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, according to this invention, the solution and catalyst of a high order silane can be mixed and the a-Si film, the poly-Si film, or the crystalline good crystal silicon film can be formed at low temperature according to an operation of a catalyst a pyrolysis or by photodissociating at high speed than before.
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TECHNICAL PROBLEM

[Description of the Prior Art] the former — formation at the low temperature of the polycrystalline silicon (henceforth "poly-Si") film, or the amorphous silicon (henceforth "a-Si") film -- plasma CVD (Chemical Vapor Deposition) — law, the heat CVD method, or the optical CVD method is used. equipment complicated [the RF generator which powder is generated in a gaseous phase with a slow membranous formation rate, and generally pollutes equipment with the plasma-CVD method from a gaseous phase], and expensive is required -- etc. — there is a problem. Moreover, in the heat CVD method from a gaseous phase, when performing membrane formation of about several micrometers at high speed, it is necessary to form membranes at temperature higher than 600 degrees C, and an expensive heat-resistant thing must be used for a substrate.
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[Table 1]

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alkali free glass etc., since a problem is in thermal resistance, membranes must be formed at temperature lower than 600 degrees C, and the crystalline good crystal silicon film cannot be obtained.

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MEANS

[Means for Solving the Problem] The technical-problem solution approach by this invention pyrolyzes the mixture of the solution of a high order silane, and a catalyst, and forms the silicon film on a substrate. Moreover, the above-mentioned mixture is photodissociated by irradiating the light of wavelength shorter than 400nm, and the silicon film is formed on a substrate.
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[0017] Moreover, what the matter containing at least one of nickel, iron, cobalt, or the platinum or its solution is used as a catalyst, and is specifically dissolved in an organic solvent at the presentation of the organic salt of nickel, a halogenation salt, etc. including nickel is desirable.
[0018] Since it is dangerous, holding a reactant high condition uses the organic solvent of a catalyst, and it should just make it mix in introductory tubing or on a substrate here, although it is possible to mix a high order silane and a catalyst directly. The organic solvent in this case has

a meltable high order silane, its reactivity with a high order silane is low, and the boiling point is a solvent lower than the boiling point of the high order silane used desirably lower than membrane formation temperature.
[0019] Although a catalyst and an organic solvent can set the combination as arbitration, as an example of a catalyst, nickel fluoride, a nickel chloride, nickel nitrate, nickel acetate, or nickel carbonate is mentioned. As an example of an organic solvent, moreover, a pentane, a hexane, a cyclohexane, The hydrocarbons expressed with CaHb(s) (5<=a<=10, 12<=b<=24), such as a heptane, an octane, an isooctane, benzene, ethylbenzene, toluene, or a xylene, diethylether, The ether and the ketones which are expressed with CaHbOc(s) (1<=a<=8, 4<=b<=14, 1<=c<=3), such as diisopropyl ether, an acetone, a methyl ethyl ketone, a methanol, ethanol, propanol, or a butanol, or alcohols is mentioned.
[0020] Moreover, the larger one of the high order silane concentration of the mixed liquor of a high order silane and a catalyst than 50 % of the weight is desirable. Since an organic solvent remains by making high order silane concentration as high as possible, the amount of the carbon incorporated in the film and oxygen can be lessened.
[0021] There is a spin coat method, a dip coating method, a spray coating method, the bar coat method, or the curtain coat method in the approach of applying a high order silane on a substrate. In the case of the spin coat method generally used, the rotational frequency of a spinner uses 300 - 6,000rpm preferably 100 to 10,000 rpm. Moreover, at this time, or it heats to the temperature higher than the boiling point of an organic solvent as spreading pretreatment, it evaporates an organic solvent beforehand and it removes an organic solvent, the polymerization of the high order silane may be carried out in part by approaches, such as an optical exposure, and you may process raising the viscosity of a high order silane etc.
[0022] Next, the predetermined silicon film is formed by the pyrolysis by heating, or the photolysis by the exposure of light. There are heating at the heater with which the base holding a substrate was equipped as the approach of heating, heating by the infrared lamp, etc. Moreover, by the approach of the photolysis by the exposure of ultraviolet radiation, it carries out in the gas ambient atmosphere where high order silanes, such as helium, neon, an argon, nitrogen, or hydrogen, are inactive. In order that a high order silane may absorb energy and may decompose as the light source of light to irradiate, the light source of ultraviolet radiation with wavelength shorter than 400nm is used. The discharge light of rare gas, such as for example, low-pressure mercury lamp light, hydrogen and heavy hydrogen or an argon, a krypton, and a xenon, excimer laser light, etc. are used for this.
[0023] If the above-mentioned approach is used, the decomposition reaction of the silane can be carried out according to an operation of a catalyst, and the silicon film can be formed at low temperature at high speed than before. In this case, if substrate temperature is higher than about 150 degrees C, the a-Si film will be obtained, and if still higher than about 500 degrees C, the poly-Si film can be obtained. In addition, the thickness of the silicon film obtained can be set as arbitration to about 5-50 micrometers by choosing the applying method.
[0024] Although the nickel mixed to a high order silane on the other hand functions as reducing the decomposition temperature of a silane, it is not desirable as a semiconductor material. For example, when using it as a solar battery, as for the nickel concentration in the film, it is desirable that it is lower than 1x1019-/cm3. It is more desirable 10-2 to 10-8 and to adjust smaller than especially 10-5 the nickel/Si ratio after dissolving the catalyst of a minute amount in an organic solvent and mixing with a high order silane especially.
[0025] Moreover, although the crystal grows from the crystalline nucleus which exists in early stages of membrane formation at the time of formation of the crystal silicon film, crystallinity will be affected when generating of a crystalline nucleus is controlled. Then, as shown in drawing 2 , on Substrate A, mixed liquor with large catalyst concentration (nickel/Si>=10-5) is applied, the 1st spreading layer B (crystalline-nucleus generating layer) is formed, and a crystalline nucleus is generated. Next, on the 1st spreading layer B, mixed liquor with small catalyst concentration (nickel/Si<10-5) is applied, and the 2nd spreading layer C is formed. The part used as the nucleus of the crystal growth to the direction of an arrow head can be restricted to the interior of the 1st spreading layer B by this, and crystalline improvement can be aimed at.

[0026] Furthermore, since a defect arises by the desorption of hydrogen at the time of the membrane formation in an elevated temperature, it decompresses to 0.01 – 10Torr extent at the time of a temperature up, and atom-like hydrogen gas is supplied to a substrate. In order to obtain the hydrogen of the shape of this atom, metals, such as an approach of obtaining hydrogen gas by high frequency discharge, such as microwave, the approach of acquiring by irradiating high energy lines, such as ultraviolet rays, at hydrogen gas, and a tungsten, are heated, and there is the approach of acquiring by contact on that front face etc. By these approaches, promotion of a polymerization and improvement in membraneous quality can be aimed at.

[Translation done.]

EXAMPLE

[Example] The example and the example of a comparison which enforced the approach of this invention and formed the silicon film hereafter are explained. Measurement shown below about the physical properties of the film formed in each example and the example of a comparison is performed, and this measurement result is shown in Table 2.
[0028] 1. Photoconductivity (A. M.1.5 or 100MW Exposure)
2. Dark Conductivity 3. Optical Gap [0029]
[Table 2]

	触媒		コート条件	膜質			
	濃度 (ppm)	量 (ml)		膜厚 (Å)	光導電率 (S/cm)	暗導電率 (S/cm)	光学ギャップ(eV)
実施例1	0. 36	0. 1	300rpm、10秒	1000	5×10^{-6}	5×10^{-10}	1. 65
実施例2	0. 36	0. 1	300rpm、10秒	800	2×10^{-4}	1×10^{-4}	1. 25
実施例3	0. 36	0. 1	300rpm、10秒	1400	2×10^{-6}	2×10^{-10}	1. 63
実施例4-1	36	1. 0	2000rpm、10秒	—	—	—	—
実施例4-2	0. 36	0. 1	100rpm、3秒	4500	3×10^{-4}	8×10^{-5}	1. 20
実施例5	0. 36	0. 1	300rpm、10秒	1500	3×10^{-6}	3×10^{-10}	1. 70
実施例6	0. 36	0. 1	300rpm、10秒	700	3×10^{-6}	1×10^{-10}	1. 72
実施例7	0. 36	0. 1	ｽﾌﾟﾚｰｺｰﾄ	15000	5×10^{-6}	4×10^{-10}	1. 64
比較例1	—	—	300rpm、10秒	成膜不可			
比較例2	—	—	300rpm、10秒	1000	5×10^{-6}	1×10^{-6}	1. 50

[0030] The configuration of the experimental device of an example 1 is shown in <example 1> drawing 1 . This experimental device is equipped with the spreading room 1 and the membrane formation room 2, and these are connected through the gate valve 3. The spreading room 1 is equipped with the spin coater 7 and exhaust air Rhine 8 which are rotated by the motor which does not hold and illustrate dropping Rhine 5 for making dropping Rhine 4 for making the solution of a high order silane dropped, and the solution of a catalyst dropped, and a substrate 6. It is combined in the middle of Rhine, and dropping Rhine 4 and 5 is led to the spreading room 1 as one Rhine. Moreover, the membrane formation room 2 is equipped with gas supply Rhine 10 and exhaust air Rhine 11 for supplying the heating heater 9 for heating a substrate 6, inert gas, etc.
[0031] In this example, what dissolved nickel fluoride in diethylether as a catalyst was used, using a PENTA silane (Si_5H_{12}) as a high order silane.
[0032] Hereafter, the formation procedure of the silicon film is explained. 0.5ml of solutions of a PENTA silane was dropped at the substrate 6 from dropping Rhine 4, and 0.05-0.5ml of solutions of nickel fluoride was made dropped from dropping Rhine 5 at the spreading room 1. And a predetermined rotational frequency or predetermined carried out time amount rotation of the spin coater 7, and the spreading film was formed. In addition, the solution of the nickel fluoride mixed to PENTA silane 1ml at this time and the monograph affair of a spin coat are shown in

Table 2.
[0033] Next, the membrane formation room 2 was introduced to 1x10-6Torr, and gaseous helium was introduced from gas supply Rhine 10 to 760Torr(s) after evacuation. Carrying out 0.5 l/min installation of the gaseous helium for a substrate 6 after migration through a gate valve 3 at the membrane formation room 2, the temperature up of the substrate 6 was carried out until it became 200 degrees C at a rate of 100 degrees C/m at the heating heater 9, substrate temperature was held for 20 minutes, and the a-Si film was formed on the substrate 6.
[0034] Carried out the temperature up of the <example 2> substrate 6, and it was heated for 60 minutes until it became 500 degrees C at a rate of 100 degrees C/m at the heating heater 9, and also it was made the same as an example 1, and the poly-Si film was formed.
[0035] The chlorination PENTA silane was used as a <example 3> high order silane, and also it was made the same as an example 1, and the a-Si film was formed.
[0036] The temperature up was carried out until it applied mixture with large catalyst concentration, it formed the 1st spreading layer B and it became 500 degrees C at a rate of 100 degrees C/m, as shown in <example 4> drawing 2 , and it heated for 10 minutes, and the crystalline nucleus was formed (Table 2 four to example 1 reference). furthermore — until it becomes temperature lower than 100 degrees C — Substrate A — mixture with small after cooling and catalyst concentration — applying — the 2nd spreading layer C — forming — 100 degrees C/m — the temperature up was carried out until it came out comparatively and became 500 degrees C, and it heated for 60 minutes — others (Table 2 four to example 2 reference) — it was made the same as an example 1, and the crystalline good crystal silicon film was formed.
[0037] As shown in <example 5> drawing 3 , instead of pyrolyzing, using the experimental device which formed the low-pressure mercury lamp 12 in the membrane formation room 2 as the light source, irradiated light with wavelength shorter than 400nm from the low-pressure mercury lamp 12, and the photolysis was carried out, and also it was made the same as an example 1, and the a-Si film was formed.
[0038] As shown in <example 6> drawing 4 , using the experimental device equipped with the microwave generating room 14 established in the membrane formation room 2 in the middle of hydrogen gas installation Rhine 13 and its Rhine 13, it decompressed to 1Torr at the time of a temperature up, and the atom-like hydrogen gas with which energy was given with the microwave generated from the microwave generating room 14 was supplied on the substrate 6, and also it was made the same as an example 1, and the a-Si film was formed.
[0039] As shown in <example 7> drawing 5 , it applied with the spray coating method by emitting a solution at the tip of the spreading room 1 side of dropping Rhine 4 and 5 with a spray gun 15 using the experimental device which formed the spray gun 15, and also it was made the same as an example 1, and the a-Si film was formed.
[0040] The silicon film was not formed, although only the solution of a high order silane was applied, without mixing the <example 1 of comparison> catalyst and also it was made the same as an example 1.
[0041] Only the solution of a high order silane was applied, without mixing the <example 2 of comparison> catalyst, and also it was made the same as an example 2, and the a-Si film was formed.
[0042] When a catalyst was not mixed like the examples 1 and 2 of a comparison from the above result, as for the silicon film, membrane formation temperature was not formed at about 200 degrees C, but the a-Si film was formed for membrane formation temperature at about 500 degrees C. On the other hand, in the membrane formation conditions especially same in the example 2 as the example 2 of a comparison, the poly-Si film was formed of the operation of a catalyst, conductivity improved, and the optical gap decreased. Moreover, in the example 4, crystallization was promoted, the crystalline good silicon film was formed, and conductivity and an optical gap improved.
[0043] In addition, this invention is not limited to the above-mentioned operation gestalt, and can add many corrections and modification to the above-mentioned operation gestalt within the limits of this invention.

[Translation done.]

* NOTICES *

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing showing the configuration of the experimental device concerning the formation approach of the silicon film of this invention
[Drawing 2] The sectional view of the crystal silicon film
[Drawing 3] Drawing showing the configuration of the experimental device of an example 5
[Drawing 4] Drawing showing the configuration of the experimental device of an example 6
[Drawing 5] Drawing showing the configuration of the experimental device of an example 7
[Description of Notations]
1 Spreading Room
2 Membrane Formation Room
4 Dropping Rhine of High Order Silane Solution
5 Dropping Rhine of Catalyst Solution
9 Heating Heater
12 Low-pressure Mercury Lamp
13 Hydrogen Gas Installation Rhine
14 Microwave Generating Room
A Substrate
B The 1st spreading layer
C The 2nd spreading layer

[Translation done.]

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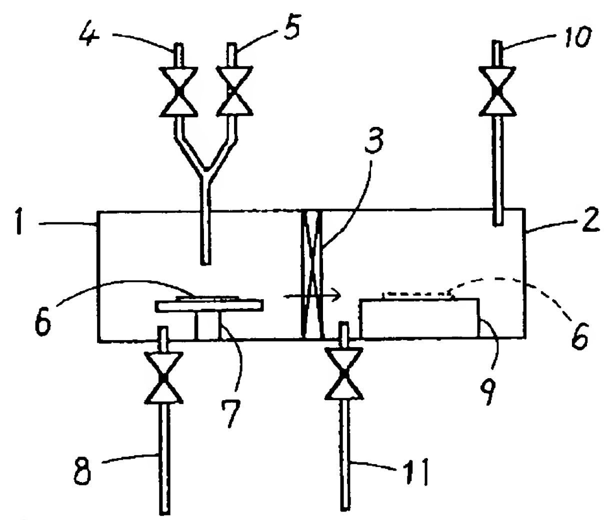
(54)【発明の名称】　シリコン膜の形成方法

(57)【要約】

【課題】　高速にかつ低温でシリコン膜を形成する方法を提供する。

【解決手段】　高次シランの溶液と触媒との混合物を基板６上に塗布して熱分解し、シリコン膜を形成する。高次シランとしては、一般式Si_nH_{2n+2}（ｎはｎ≧３の整数）で表される高次シラン、または一般式$Si_nH_lX_m$（Ｘは塩素、フッ素、臭素またはヨウ素のいずれかであり、ｌ＋ｍ＝２ｎ＋２、ｎはｎ≧３の整数）で表されるハロゲン化高次シランを用いる。触媒としては、ニッケル、鉄、コバルトまたは白金の少なくとも一つを含有する物質または溶液からなるものを用いる。



【特許請求の範囲】

【請求項１】　高次シランの溶液と触媒との混合物を熱分解して、シリコン膜を基板上に形成することを特徴とするシリコン膜の形成方法。

【請求項２】　高次シランの溶液と触媒との混合物を４００ｎｍより短い波長の光を照射することにより光分解して、シリコン膜を基板上に形成することを特徴とするシリコン膜の形成方法。

【請求項３】　前記高次シランは、一般式Si_nH_{2n+2}（ｎはｎ≧３の整数）で表される高次シラン、または一般式$Si_nH_lX_m$（Ｘは塩素、フッ素、臭素またはヨウ素のいずれかであり、ｌ＋ｍ＝２ｎ＋２、ｎはｎ≧３の整数）で表されるハロゲン化高次シランであることを特徴とする請求項１または２記載のシリコン膜の形成方法。

【請求項４】　前記触媒は、ニッケル、鉄、コバルトまたは白金の少なくとも一つを含有する物質または溶液からなることを特徴とする請求項１または２記載のシリコン膜の形成方法。

【請求項５】　前記触媒の溶媒は、高次シランが可溶でありかつ沸点がシリコン膜の形成時の温度より低い溶媒であることを特徴とする請求項４記載のシリコン膜の形成方法。

【請求項６】　触媒濃度の大きい混合物を基板上に塗布して結晶核発生層を形成し、この上に触媒濃度の小さい混合物を塗布することを特徴とする請求項１ないし５のいずれかに記載のシリコン膜の形成方法。

【請求項７】　熱分解または光分解する際に基板に原子状の水素ガスを供給することを特徴とする請求項１ないし６のいずれかに記載のシリコン膜の形成方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、太陽電池や薄膜トランジスタ等の半導体デバイスに用いられるシリコン膜の形成方法に関する。

【０００２】

【従来の技術および発明が解決しようとする課題】従来より、多結晶シリコン（以下「poly－Ｓｉ」という。）膜やアモルファスシリコン（以下「ａ－Ｓｉ」という。）膜の低温での形成には、プラズマＣＶＤ（Chemical Vapor Deposition）法、熱ＣＶＤ法または光ＣＶＤ法等が用いられている。一般に、気相からのプラズマＣＶＤ法では、膜の形成速度が遅い、気相中で粉末が発生し装置を汚染する、高周波発生装置等の複雑で高価な装置が必要である等の問題がある。また、気相からの熱ＣＶＤ法では、高速で数μｍ程度の成膜を行う場合、６００℃より高い温度で成膜する必要があり、基板には高価な耐熱性のものを用いなければならない。

【０００３】また、上記の方法の他に、ニッケル等の金属を触媒にしてａ－Ｓｉを低温で固相結晶化させる方法（特開平６－２４４１０３号公報参照）もあるが、膜の形成速度が遅いため厚膜の形成には適さない。

【０００４】そこで、これらの欠点を解消する液相からの膜形成方法として、基板に高次シラン液を塗布し紫外光照射により成膜を行う方法（特開平５－１４４７４１号公報参照）や、基板に高次シラン液を塗布し昇温過程を含む熱履歴を経ることにより成膜を行う方法（特開平７－２６７６２１号公報参照）が提案されている。

【０００５】しかし、これらの方法では、基板の温度を適切な成膜温度に設定すると、高次シランの沸点が低いために（表１参照）、重合が完了する前に高次シランが蒸発し、１μｍより厚い膜の形成や所望の膜厚の調整が困難となる。

【０００６】

【表１】

	SiH_4	Si_2H_6	Si_3H_8	n-Si_4H_{10}	n-Si_5H_{12}	n-Si_6H_{14}	n-Si_7H_{16}
融点(℃)	-185	-132.5	-117.4	-89.9	-72.2	-44.7	-30.1
沸点(℃)	-111.9	-14.5	52.9	108.1	153.2	193.6	226.8

【０００７】一般に、高次シラン液を塗布することにより液相から成膜する方法は、気相から成膜する方法に比べ高速に成膜することができる。しかし、上述のように高次シランは沸点が低いために成膜時に高次シラン液が蒸発し、成膜された膜が塗布膜厚よりかなり薄くなり、任意の膜厚を得ることができない。このため、成膜を高速に行いかつ低温での反応性を向上させることが望まれていた。

【０００８】また、比較的結晶性の良い結晶シリコン膜を高速に形成するには、一般に６００℃より高い温度で成膜する必要がある。しかし、例えば、無アルカリガラス等からなる安価な基板を利用しようとすれば、耐熱性に問題があるため６００℃より低い温度で成膜しなければならず、結晶性の良い結晶シリコン膜を得られない。

【０００９】そこで、本発明の目的は、上記問題点に鑑み、デバイスとしての品質を維持した上で、高速にかつ低温でシリコン膜を形成する方法を提供することである。

【００１０】

【課題を解決するための手段】本発明による課題解決方法は、高次シランの溶液と触媒との混合物を熱分解して、シリコン膜を基板上に形成するものである。また、上記混合物を４００ｎｍより短い波長の光を照射することにより光分解して、シリコン膜を基板上に形成するも

のである。

【００１１】高次シランとしては、一般式Si_nH_{2n+2}（ｎはｎ≧３の整数）で表される高次シラン、または一般式$Si_nH_lX_m$（Ｘは塩素、フッ素、臭素またはヨウ素のいずれかであり、ｌ＋ｍ＝２ｎ＋２、ｎはｎ≧３の整数）で表されるハロゲン化高次シランを用いればよい。また、触媒としては、ニッケル、鉄、コバルトまたは白金の少なくとも一つを含有する触媒またはこの触媒の溶液からなるものを用い、溶液の場合、触媒の溶媒は、高次シランが可溶でありかつ沸点がシリコン膜の形成時の温度より低いものであればよい。この方法によれば、触媒の作用によりシランを分解反応させて、従来より高速にかつ低温で所望の厚さのシリコン膜を形成することができる。

【００１２】特に、結晶シリコン膜の形成においては、触媒濃度の大きい混合物を基板上に塗布して結晶核発生層を形成し、この上に触媒濃度の小さい混合物を塗布するようにすれば、良好な結晶を成長させることができる。

【００１３】また、熱分解または光分解する際に基板に原子状の水素ガスを供給するようにすれば、重合の促進および膜質の向上を図ることができる。

【００１４】

【発明の実施の形態】以下、本発明の実施の形態を詳細に説明する。

【００１５】本発明によりシリコン膜を形成するには、まず、不活性ガス雰囲気中に置かれたガラス等の基板に高次シランの溶液と触媒との混合物を塗布する。あるいは、高次シランの溶液と触媒の溶液との混合物を塗布するようにしてもよい。

【００１６】高次シランとしては、一般式Si_nH_{2n+2}（ｎはｎ≧３の整数）で表されるものが用いられ、具体的には、トリシラン（Si_3H_8）、テトラシラン（Si_4H_{10}）、ペンタシラン（Si_5H_{12}）、ヘキサシラン（Si_6H_{14}）、ヘプタシラン（Si_7H_{16}）、オクタシラン（Si_8H_{18}）、ノナシラン（Si_9H_{20}）等である。高次シランに代わり、一般式$Si_nH_lX_m$（Ｘは塩素、フッ素、臭素またはヨウ素のいずれかであり、ｌ＋ｍ＝２ｎ＋２、ｎはｎ≧３の整数）で表される、例えば、塩化ペンタシラン等のハロゲン化高次シランであってもよい。また、高次シランまたはハロゲン化高次シランは２種以上用いてもよい。

【００１７】また、触媒としては、ニッケル、鉄、コバルトまたは白金の少なくとも一つを含有する物質あるいはその溶液が用いられ、具体的にはニッケルの有機塩、ハロゲン化塩等の組成にニッケルを含み、有機溶媒に１ppbより多く溶解するものが望ましい。

【００１８】ここで、高次シランと触媒とを直接混合することは可能であるが、反応性の高い状態を保持するのは危険であるために、触媒の有機溶媒を用いて導入管中もしくは基板上で混合させればよい。この場合の有機溶媒は、高次シランが可溶で高次シランとの反応性が低く、沸点が成膜温度より低い、望ましくは使用する高次シランの沸点より低い溶媒である。

【００１９】触媒と有機溶媒とはその組み合わせを任意に設定することができるが、触媒の例としてはフッ化ニッケル、塩化ニッケル、硝酸ニッケル、酢酸ニッケルまたは炭酸ニッケル等が挙げられる。また、有機溶媒の例としては、ペンタン、ヘキサン、シクロヘキサン、ヘプタン、オクタン、イソオクタン、ベンゼン、エチルベンゼン、トルエンまたはキシレン等のC_aH_b（５≦ａ≦１０，１２≦ｂ≦２４）で表される炭化水素類やジエチルエーテル、ジイソプロピルエーテル、アセトン、メチルエチルケトン、メタノール、エタノール、プロパノールまたはブタノール等の$C_aH_bO_c$（１≦ａ≦８，４≦ｂ≦１４，１≦ｃ≦３）で表されるエーテル類、ケトン類またはアルコール類が挙げられる。

【００２０】また、高次シランと触媒との混合液の高次シラン濃度は５０重量％より大きい方が好ましい。高次シラン濃度を可能な限り高くすることにより有機溶媒が残留するので、膜中に取り込まれる炭素、酸素の量を少なくすることができる。

【００２１】基板上に高次シランを塗布する方法には、スピンコート法、ディップコート法、スプレーコート法、バーコート法またはカーテンコート法等がある。一般に用いられているスピンコート法の場合、スピナーの回転数は１００～１０，０００rpm、好ましくは３００～６，０００rpmを用いる。また、このとき、塗布前処理として有機溶媒の沸点より高い温度に加熱して、予め有機溶媒を蒸発させて有機溶媒の除去を行う、あるいは光照射等の方法により一部高次シランを重合させて高次シランの粘度を上昇させる等の処理を行ってもよい。

【００２２】次に、加熱による熱分解、あるいは光の照射による光分解等により所定のシリコン膜を形成する。加熱の方法としては、基板を保持する台に備えられたヒーターによる加熱や赤外線ランプによる加熱等がある。また、紫外光の照射による光分解の方法では、ヘリウム、ネオン、アルゴン、窒素または水素等の高次シランとは不活性なガス雰囲気中にて行う。照射する光の光源としては、高次シランがエネルギーを吸収して分解するために、波長が４００ｎｍより短い紫外光の光源が用いられる。これには、例えば、低圧水銀ランプ光、水素や重水素、あるいはアルゴン、クリプトン、キセノン等の希ガスの放電光、エキシマレーザ光等が用いられる。

【００２３】上記の方法を用いると、触媒の作用によりシランを分解反応させて、従来より高速にかつ低温でシリコン膜を形成することができる。この場合、基板温度が約１５０℃より高いとａ－Ｓi膜を得、さらに約５００℃より高いとpoly－Ｓi膜を得ることができる。なお、得られるシリコン膜の膜厚は塗布法を選択すること

により、５～５０μm程度まで任意に設定することができる。

【００２４】一方、高次シランに混合するニッケルは、シランの分解温度を低下させるように機能するが、半導体材料としては好ましくない。例えば、太陽電池として使用する場合には、膜中のニッケル濃度は1×10^{19}／cm^3より低いことが望ましい。特に、有機溶媒に微量の触媒を溶解させ、高次シランと混合した後のＮｉ／Ｓｉ比を10^{-2}～10^{-8}、特に10^{-5}より小さく調整するのがより好ましい。

【００２５】また、結晶シリコン膜の形成時には、成膜初期に存在する結晶核から結晶が成長していくが、結晶核の発生を制御すると結晶性に影響を与えることになる。そこで、図２に示すように、基板Ａ上に触媒濃度の大きい混合液（Ni／Si$\geqq10^{-5}$）を塗布して第１塗布層Ｂ（結晶核発生層）を形成し、結晶核を生成する。次に、第１塗布層Ｂの上に触媒濃度の小さい混合液（Ｎｉ／Ｓｉ$<10^{-5}$）を塗布し、第２塗布層Ｃを形成する。これにより、矢印方向への結晶成長の核となる部分を第１塗布層Ｂの内部に制限でき、結晶性の向上を図ることができる。

【００２６】さらに、高温での成膜時には水素の脱離により欠陥が生じるため、昇温時に０.０１～１０Torr程度まで減圧を行い、基板に原子状の水素ガスを供給する。この原子状の水素を得るには、例えば、水素ガスをマイクロ波等の高周波放電により得る方法、水素ガスに紫外線等の高エネルギー線を照射することにより得る方法、タングステン等の金属を加熱し、その表面との接触により得る方法等がある。これらの方法により、重合の促進および膜質の向上を図ることができる。

【００２７】

【実施例】以下、本発明の方法を実施してシリコン膜を形成した実施例および比較例を説明する。各実施例、比較例で成膜された膜の物性について以下に示す測定を行い、この測定結果を表２に示す。

【００２８】１．光導電率（A.M. １.５、１００mW照射）

２．暗導電率

３．光学ギャップ

【００２９】

【表２】

	触媒		コート条件	膜質			
	濃度 (ppm)	量 (ml)		膜厚 (Å)	光導電率 (S/cm)	暗導電率 (S/cm)	光学ギャップ(eV)
実施例1	0.36	0.1	300rpm、10秒	1000	5×10^{-6}	5×10^{-10}	1.65
実施例2	0.36	0.1	300rpm、10秒	800	2×10^{-4}	1×10^{-4}	1.25
実施例3	0.36	0.1	300rpm、10秒	1400	2×10^{-6}	2×10^{-10}	1.63
実施例4-1	36	1.0	2000rpm、10秒	—	—	—	—
実施例4-2	0.36	0.1	100rpm、3秒	4500	3×10^{-4}	8×10^{-5}	1.20
実施例5	0.36	0.1	300rpm、10秒	1500	3×10^{-6}	3×10^{-10}	1.70
実施例6	0.36	0.1	300rpm、10秒	700	3×10^{-6}	1×10^{-10}	1.72
実施例7	0.36	0.1	スプレーコート	15000	5×10^{-6}	4×10^{-10}	1.64
比較例1	—	—	300rpm、10秒	成膜不可			
比較例2	—	—	300rpm、10秒	1000	5×10^{-6}	1×10^{-8}	1.50

【００３０】＜実施例１＞図１に、実施例１の実験装置の構成を示す。この実験装置は、塗布室１および成膜室２を備え、これらはゲートバルブ３を介してつながれている。塗布室１には、高次シランの溶液を滴下させるための滴下ライン４、触媒の溶液を滴下させるための滴下ライン５、基板６を保持し図示しないモータにより回転されるスピンコーター７および排気ライン８が備えられている。滴下ライン４，５はラインの途中で結合されており、１本のラインとして塗布室１に導かれている。また、成膜室２には、基板６を加熱するための加熱ヒーター９、不活性ガス等を供給するためのガス供給ライン１０および排気ライン１１が備えられている。

【００３１】この実施例では、高次シランとしてペンタシラン（Si_5H_{12}）を用い、触媒としてフッ化ニッケルをジエチルエーテルに溶解したものを用いた。

【００３２】以下、シリコン膜の形成手順を説明する。塗布室１において、基板６にペンタシランの溶液を滴下ライン４から０.５ml滴下し、フッ化ニッケルの溶液を滴下ライン５から０.０５～０.５ml滴下させた。そして、スピンコーター７を所定の回転数または所定の時間回転させて、塗布膜の形成を行った。なお、このときのペンタシラン１mlに混合するフッ化ニッケルの溶液およびスピンコートの各条件を表２に示す。

【００３３】次に、成膜室２を1×10^{-6} Torrまで真空排気後、ガス供給ライン１０からヘリウムガスを７６０Torrまで導入した。基板６を成膜室２にゲートバル

ブ３を通して移動後、ヘリウムガスを０.５１／min導入しながら、基板６を加熱ヒーター９で毎分１００℃の割合で２００℃になるまで昇温し、２０分間基板温度を保持して基板６上にａ－Ｓi膜を形成した。

【００３４】＜実施例２＞基板６を加熱ヒーター９で毎分１００℃の割合で５００℃になるまで昇温し、６０分間加熱した他は実施例１と同じにして、poly－Ｓi膜を形成した。

【００３５】＜実施例３＞高次シランとして塩化ペンタシランを用いた他は実施例１と同じにして、ａ－Ｓi膜を形成した。

【００３６】＜実施例４＞図２に示すように、触媒濃度の大きい混合物を塗布し第１塗布層Ｂを形成して、毎分１００℃の割合で５００℃になるまで昇温し、１０分間加熱して結晶核を形成した（表２では実施例４－１参照）。さらに、１００℃より低い温度になるまで基板Ａを冷却後、触媒濃度の小さい混合物を塗布し第２塗布層Ｃを形成し、毎分１００℃の割合で５００℃になるまで昇温し、６０分間加熱した（表２では実施例４－２参照）他は実施例１と同じにして、結晶性の良い結晶シリコン膜を形成した。

【００３７】＜実施例５＞図３に示すように、熱分解する代わりに、成膜室２に光源として低圧水銀ランプ１２を設けた実験装置を用いて、低圧水銀ランプ１２から波長が４００ｎｍより短い光を照射して光分解をした他は実施例１と同じにして、ａ－Ｓi膜を形成した。

【００３８】＜実施例６＞図４に示すように、成膜室２に水素ガス導入ライン１３とそのライン１３の途中に設けられたマイクロ波発生室１４とを備えた実験装置を用いて、昇温時に１Torrまで減圧を行い、マイクロ波発生室１４から発生するマイクロ波でエネルギーが与えられた原子状の水素ガスを基板６上に供給した他は実施例１と同じにして、ａ－Ｓi膜を形成した。

【００３９】＜実施例７＞図５に示すように、滴下ライン４，５の塗布室１側先端にスプレーガン１５を設けた実験装置を用いて、スプレーガン１５で溶液を放射することによるスプレーコート法によって塗布した他は実施例１と同じにして、ａ－Ｓi膜を形成した。

【００４０】＜比較例１＞触媒を混合せずに高次シランの溶液のみを塗布した他は実施例１と同じにしたが、シリコン膜は形成されなかった。

【００４１】＜比較例２＞触媒を混合せずに高次シランの溶液のみを塗布した他は実施例２と同じにして、ａ－Ｓi膜を形成した。

【００４２】以上の結果から、比較例１，２のように触媒を混合しない場合には、成膜温度が約２００℃ではシ

リコン膜は形成されず、成膜温度が約５００℃ではａ－Ｓi膜が形成された。これに対し、特に実施例２では比較例２と同じ成膜条件において、触媒の作用によりpoly－Ｓi膜が形成され、導電率が向上し光学ギャップが減少した。また、実施例４では結晶化が促進されて結晶性の良好なシリコン膜が形成され、導電率および光学ギャップが向上した。

【００４３】なお、本発明は、上記実施形態に限定されるものではなく、本発明の範囲内で上記実施形態に多くの修正および変更を加え得ることができる。

【００４４】

【発明の効果】以上のように、この発明によると、高次シランの溶液と触媒とを混合させて熱分解または光分解することにより、触媒の作用によって従来より高速にかつ低温でａ－Ｓi膜、poly－Ｓi膜または結晶性の良好な結晶シリコン膜を形成することができる。

【００４５】また、この方法により成膜温度が低温化されることにより、安価な基板を採用することができる。

【００４６】特に、結晶シリコン膜の形成においては、触媒濃度の大きい混合物を基板上に塗布して結晶核発生層を形成し、この上に触媒濃度の小さい混合物を塗布するようにすれば、結晶シリコン膜の結晶性の向上を図ることができる。

【００４７】また、熱分解または光分解する際に基板に原子状の水素ガスを供給するようにすれば、重合の促進および膜質の向上を図ることができる。

【図面の簡単な説明】

【図１】本発明のシリコン膜の形成方法に係る実験装置の構成を示す図

【図２】結晶シリコン膜の断面図

【図３】実施例５の実験装置の構成を示す図

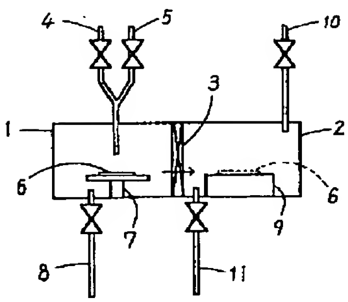
【図４】実施例６の実験装置の構成を示す図

【図５】実施例７の実験装置の構成を示す図

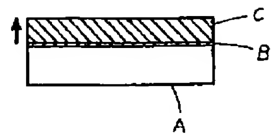
【符号の説明】

１　塗布室
２　成膜室
４　高次シラン溶液の滴下ライン
５　触媒溶液の滴下ライン
９　加熱ヒーター
１２　低圧水銀ランプ
１３　水素ガス導入ライン
１４　マイクロ波発生室
Ａ　基板
Ｂ　第１塗布層
Ｃ　第２塗布層

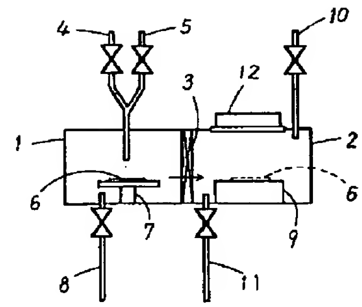
【図１】


4
5
10
3
1
2
6
6
7
9
8
11

【図２】


C
B
A

【図３】


4
5
10
12
3
1
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6
6
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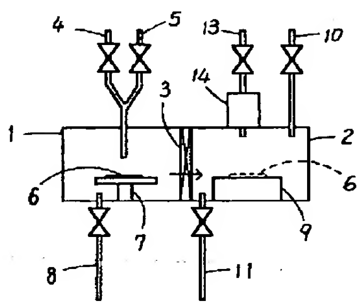
9
8
11

【図４】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14
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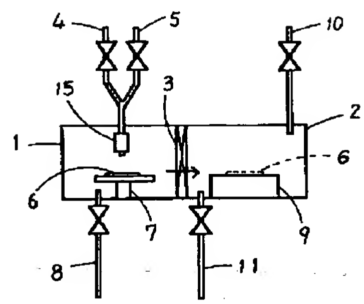
【図５】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